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A MOLECULAR COMPLEX MODEL FOR THE
CHEMISORPTION OF HYDROGEN ON A NICKEL SURFACE

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I. INTRODUCTION

We present here some preliminary results of the application of atomic pseudopotentials to the construction of a simple model of the chemisorption of hydrogen molecules on a transition metal surface. The experimental facts which must be understood are the following: (1) Nickel chemisorbs hydrogen molecules dissociatively down to liquid nitrogen temperature [1]. The reaction is considered to take place with little or no activation energy. (2) Copper which is similar to nickel except that it contains a filled 3d band does not dissociatively chemisorb hydrogen molecules, although copper strongly absorbs hydrogen atoms [2]. The ability of nickel to dissociatively chemisorb hydrogen is generally ascribed to the unfilled d band of the nickel. The aim of this investigation is to understand the role of the electronic structure of a transition metal, particularly the d electrons, in determining its catalytic activity.

The model which we propose to investigate considers the processes of chemisorption to be adequately described to first order in terms of a local, strongly coupled surface complex,



A model of this type was first put forward over forty years ago by Eyring and his collaborators [3] in a valence bond

approximation. They computed an activation energy of approximately one electron volt. More recently the model has been investigated by H. Deuss and A. van der Avoird [4], who studied the effect of a single nickel 3d or 4s electron, the remainder of the nickel atomic core being treated by a point charge model. The 3d electrons caused an unactivated dissociative chemisorption, while the 4s electrons alone do not chemisorb a hydrogen molecule unless a high activation energy barrier is surmounted. While both computations are informative, the number of approximations made is so great as to render any interpretation of the results extremely tenuous. In addition, it has been shown that although only d-electron metals adsorb H_2 , the adsorption strength is not directly related to the amount of d-character, so that van der Avoird's approximation of d-electron binding to the hydrogen is clearly oversimplified.

In our study of the surface complex model of chemisorption we have investigated a limited portion of the potential energy surface of reaction (1). The calculations have been carried out using a large Gaussian basis set in both the Hartree-Fock-self-consistent-field (SCF) and the generalized-valence-bond (GVB) [5] approximations. In addition, the argon core of the nickel atom has been replaced by an accurate, ab initio pseudopotential developed by Melius, Kahn, and Goddard [6]. It is the introduction of this pseudopotential which has made it possible to investigate a problem of this magnitude and complexity.

II. RESULTS and DISCUSSION

Since little information is available in the literature concerning the electronic structure of either NiH [7] or Ni₂ [8], we begin with a brief summary of our computations on these species as a fuller discussion will be published elsewhere [9]. We performed SCF computations on the ground $^2\Delta$ ($\delta^3\pi^41\sigma^22\sigma^2$) and first two excited states, $^2\pi$ ($\delta^4\pi^31\sigma^22\sigma^2$) at 0.59 eV and $^2\Sigma$ ($\delta^4\pi^41\sigma^22\sigma^1$) at 1.49 eV of NiH ($R = 1.48 \text{ \AA}$). The orbital energies and a Mulliken population analysis of the ground $^2\Delta$ state are presented in Table 1. The population analysis shows large Ni (9.76) to H (1.24) charge transfer. At the same time the sigma bonding orbitals are quite delocalized showing extensive Ni (3d) - H (1s) bonding, as well as Ni 3d-4s hybridization. However, when we performed a GVB computation on the $^2\Delta$ ground state allowing the sigma electrons to correlate, the Ni 3d electrons localize and the NiH bond is best described as a two electron Ni (4s) - H (1s) bond.

The situation for the Ni₂ ($R = 2.49 \text{ \AA}$) molecule is similar to, although more complex than, that of NiH. If we consider a Ni atom in the d^9s configuration, it is possible to construct on the order of 30 electronic states by properly coupling the d "hole" on the two Ni atoms. As for NiH the lowest electronic state arises from a configuration containing two "holes" in the δ shell ($\delta_u^3\delta_g^3\pi_u^4\pi_g^41\sigma_g^22\sigma_g^21\sigma_u^2$).

The spread in energy between this electronic state and one containing two "holes" in the σ shell ($\delta_u^4 \delta_g^4 \pi_u^4 \pi_g^4 1\sigma_g^2 2\sigma_g^1 1\sigma_u^1, {}^3\Sigma_u$) is 0.54 eV. In Table 2 we tabulate the results of a SCF calculation on the ${}^3\Sigma_u$ state of Ni_2 . While this state is not the ground electronic state it may be represented by a single determinantal function and was thus accessible to computation as a pure electronic state by our SCF programs unlike the mixed states arising from "holes" in the δ or π shells. The Mulliken population analysis presented in Table 2 reinforces the conclusion drawn from the NiH results that the 3d electrons are localized and do not participate significantly in the Ni-Ni bond. This bond may be represented to a high order of approximation as a two electron Ni (4s) - Ni (4s) sigma bond. In this model the 3d electrons are postulated to act as a small perturbation which determines the order of the electronic states but not the character of the metallic bonding. Based on this hypothesis Melius [10] has developed an atomic pseudopotential for Ni^+ for which a single 4s electron moves in the spherically averaged field of nine 3d electrons as well as the argon core. The Ni_2 computation can thus be reduced to a two electron problem ($1\sigma_g^2$, $\Sigma = - .2038$). The results of Table 2 also indicate that even diatomic Ni_2 is beginning to show properties characteristic of the bulk metal. The 3d "band width" computed as the difference in energy between the $1\delta_u$ and $2\sigma_g$ eigenvalues (3.5 eV) is close to the experimental band theory value of 3.3 eV [11].

There has recently appeared a study of the bonding of ethylene to Ni_2 in the SCF, χ_α , Scattered-Wave approximation by Rosch and Rhodin [12]. They found the ground state of Ni_2 to be $^1\Sigma_g (\delta_u^4 \delta_g^4 \pi_u^4 \pi_g^4 1\sigma_g^2 2\sigma_g^2)$. We repeated their SCF- χ_α -SW computation and examined the character of the sigma orbitals. The $1\sigma_g$ was primarily Ni 3d with some Ni 4s population while the $2\sigma_g$ was Ni 4s in character hybridized with Ni 3d. We computed the energy of this $^1\Sigma_g$ state in the SCF approximation and found the energy to be 7.1 eV above that of the $^3\Sigma_u$ state reported above. In addition, the sigma orbitals exhibited the same Ni 3d-4s hybridization and delocalization as the SCF- χ_α -SW computation. We also performed a GVB computation on the $^1\Sigma_g^+$ state, $1\sigma_g^2 (1\sigma_u^2 - \lambda 2\sigma_g^2)$. The energy of this state was slightly lower than that of the $^3\Sigma_u$ state. The $1\sigma_g$ orbital remained a Ni (4s) - Ni (4s) two electron bond, while the 3d electrons were localized, one on the left and the other on the right nickel atom.

The model we have chosen for the chemisorption of hydrogen on a nickel surface is illustrated in Figure 1. The Ni_2 bond length of 2.49 Å was taken equal to the nearest neighbor distance in bulk nickel while the distance, D , was taken equal to the length of the NiH bond, 1.48 Å. The H_2 distance, R_1 , was then varied from 0.74 Å to 2.49 Å in order to follow the path of the dissociative chemisorption reaction, equation (1).

In the C_{2v} approach of our model the reactants $\text{H}_2 (^1\Sigma_g)$ and $\text{Ni}_2 (^3\Sigma_u)$ correlate with one 3B_1 state of Ni_2H_2 ,

$$-5a_1^1-2a_2^2-3b_1^1-2b_2^2 \quad , \quad (2)$$

while the products $2NiH (^2\Delta)$ correlate with another 3B_1 state,

$$-4a_1^1-2a_2^2-4b_1^1-2b_2^2 \quad , \quad (3)$$

where only the highest occupied orbital of each symmetry is indicated. In the sense of the Woodward-Hoffman [13] rules of the analysis of Longuet-Higgins and Abrahamson [14] this change of orbital symmetry as we go from reactants to products must give rise to an activation energy barrier. This is most easily seen if we adopt the viewpoint that the nickel 3d electrons are essentially localized and that the reaction proceeds by the breaking of two single bonds of the reactants ($1a_1^2 2a_1^2$) and the formation of two single bonds of the products ($1a_1^2 1b_1^2$). The correlation diagram for this simple model is given in Figure 2. The change in orbital symmetry is clearly seen on both the orbital correlation diagram, Figure 2a, and the state correlation diagram, Figure 2b. In addition the state correlation diagram suggests the possibility that the reaction might take place through the singlet-triplet splitting of the excited B_1 state.

It should be noted that the reaction path that we have chosen is not the path of least energy as studies of the bimolecular exchange reaction of H_2 have indicated [15]. It

was chosen as a representative path that would provide semi-quantitative information about the role of the 3d electrons in the dissociative chemisorption process.

We have performed an SCF calculation on the 3B_1 state of the Ni_2H_2 complex for several points along the reaction path described in Figure 1. In Table 3 we present the orbital energies and Mulliken population analysis for the a_1 and b_1 molecular orbitals for two H_2 distances, $R_1 = 0.74$ and $R_2 = 2.49 \text{ \AA}$. The other occupied orbitals are essentially 3d in character and are therefore not tabulated. The results of the population analysis clearly show that at R_1 :

(1) the Ni_2H_2 complex can be considered to consist of a weakly interacting Ni_2 and H_2 molecule; (2) the 3d electrons are localized; (3) a slight Ni to H charge transfer takes place; (4) a four electron model, $1a_1^2 4a_1^2$, should adequately represent the Ni_2 and H_2 bonds. In addition, the population analysis indicates that the d "hole" in the $5a_1$, and $3b_1$ orbitals is perpendicular to the Ni_2 axis. When the hydrogen distance is R_2 , the picture that may be constructed from the population analysis is similar but not as clearly defined as in the case of R_1 . In particular, the four electron model, $3a_1^2 3b_1^2$, is a less satisfactory approximation to the bonding and the 3d electrons participate slightly in the Ni - H bond ($2a_1, 2b_1$). In this limit the d "hole" in the $4a_1$ and $4b_1$ orbitals is now perpendicular to the NiH axis. We have also performed an SCF calculation for the 3B_1 state of Ni_2H_2 at

an arbitrarily chosen hydrogen distance, $R_3 = 1.06 \text{ \AA}$, which resulted in a barrier height to dissociation of 1.22 eV.

In order to separate the role of the 3d and 4s electrons we carried out a series of calculations based on the four electron model with the Ni^+ pseudopotential in both the SCF and GVB approximations. In Table 4 we present the barrier height, ΔE , computed as the difference in energy of the Ni_2H_2 complex for two H_2 distances, $R_1 = 0.74 \text{ \AA}$ and $R_3 = 1.06 \text{ \AA}$. The results are compared with the full twenty-two electron SCF calculation discussed above. In the case of the GVB calculations, both electron pairs were correlated thus allowing both "right-left" and "front-back" correlation within the four electron model. The results show that the barrier is lowered 0.45 eV when the 3d electrons are allowed to adjust their charge distribution by rotating so that the 3d "hole" remains perpendicular to either the Ni_2 or NiH bond as the reaction proceeds. It should be remembered that within the four electron model the nine 3d electrons are represented by a spherically averaged potential and the model is somewhat analogous to the case of copper with a filled 3d shell. The barrier is lowered approximately the same amount, 0.47 eV, when the two electron pairs are correlated within the GVB approximation. If the two effects are considered additive, an activation energy barrier of approximately 0.75 eV remains. Part of this barrier might be removed by either allowing the charge distribution of our two nickels to be polarized by the

surrounding surface or by picking a more suitable reaction path. In fact, at the hydrogen distance, R_3 , the triplet configuration $(1a_1^2 2a_1^1 1b_1^1)$ lies 0.3 eV lower than the singlet configuration $(1a_1^2 2a_1^2)$. The reaction surface is thus far more complex than our simple model would seem to indicate. Further work on exploring the reaction surface is in progress as well as a study of the effect of allowing electron correlation of the bonding pairs within a full twenty-two electron GVB calculation.

III. CONCLUSIONS

The most striking conclusions to be drawn from this localized model of chemisorption on a transition metal surface are as follows: (1) The 3d electrons in both Ni_2 and NiH are quite localized and atomic like in character. The metallic bond in Ni_2 and the hydride bond in NiH are predominantly Ni (4s) in origin and may be adequately represented as a two electron sigma bond. (2) The manifold of electronic states within a half of an electron volt of the ground state of Ni_2 is both dense and complex. By extension the situation is similar above the metallic surface. (3) The Ni 3d electrons take part in the catalytic process by providing a mechanism (expansion or contraction and rotation of the 3d orbitals) by which charge may be redistributed within the bonding region as the hydrogen approaches the surface and thereby lowering the barrier to reaction as one set of bonds is broken and another formed. Thus, the d-electrons participate only minimally in the actual bond. This fact which is apparent from our Mulliken populations in Table 3, is in agreement with the fact that the d-electron character of a metal is not simply related to adsorption strength and that hydrogen atoms will adsorb even on non-transition metals. In addition the singly occupied d orbitals on different centers can recouple with each other during the reaction process in order to change their spin and spatial

symmetry. This recoupling mechanism allows the reaction to proceed on alternate reaction paths which have lower activation barriers (3B_1 state of Figure 2). (4) The adsorbed hydrogen is found to be hydridic (Table 3) in agreement with electro-negativity arguments.

The role of the 3d electrons in catalytic activity is seen to be both subtle and complex. Two further areas for investigation are immediately apparent. First, larger metallic clusters must be constructed in order to more adequately model the reactive surface. Second, other representative transition metals both to the left of nickel and in the second and third row must be studied in order to see if the localized model of the d-electrons presented here holds throughout the periodic table. Work in these areas is currently in progress in our respective laboratories.

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TABLE 1.

Orbital energies and Mulliken population analysis of the $^2\Delta$ state of NiH, $R = 1.48 \text{ \AA}$. Energies in Hartrees.

Orbital Energies	Ni			H	
	4s	4p	3d	1s	2p
2 σ -.303	.93	.11	.41	.54	.01
1 σ -.440	-.03	-.01	1.38	.65	.00
1 π -.452	—	.01	3.95	—	.04
1 δ -.498	—	—	3.00	—	—
Total Population	.91	.10	8.74	1.19	.06

TABLE 2.

Orbital energies and Mulliken population analysis of the $^3\Sigma_u$ state of Ni_2 , $R = 2.49 \text{ \AA}$. Energies in Hartrees.

Orbital Energies	Ni		
	4s	4p	3d
$1\sigma_g$ -.209	.92	.08	.00
$1\delta_u$ -.358	—	—	2.0
$1\delta_g$ -.362	—	—	2.0
$1\pi_g$ -.392	—	—	1.99
$1\pi_u$ -.413	—	—	1.99
$1\sigma_u$ -.450	.00	.01	.49
$2\sigma_g$ -.488	.01	.00	.49
Total Population	.93	.11	8.96

TABLE 3.

Orbital energies and Mulliken population analysis of the 3B_1 state of Ni_2H_2 at H_2 distances, $R_1 = 0.74 \text{ \AA}$ and $R_2 = 2.49 \text{ \AA}$, and $d = 1.48 \text{ \AA}$. Population of filled a_2 and b_2 orbitals included in total population. Energies in Hartrees.

$R_1 = 0.74 \text{ \AA}$		Ni			H	
Orbital	Energies	4s	4p	3d	1s	2p
$1a_1$	-.706	.02	.01	.04	.88	.03
$2a_1$	-.425	.00	.00	.97	.02	.01
$3a_1$	-.408	.02	.01	.95	.02	.00
$4a_1$	-.176	.84	.10	.01	.01	.04
$5a_1$	-.524	.00	.01	.49	.00	.00
$1b_1$	-.417	.00	.01	.98	-.04	.04
$2b_1$	-.386	.04	-.01	.92	.03	.02
$3b_1$	-.525	.01	.00	.49	.00	.00
Total Population		.93	.13	8.84	.92	.18

$R_2 = 2.49 \text{ \AA}$		Ni			H	
Orbital	Energies	4s	4p	3d	1s	2p
$1a_1$	-.476	.00	.01	.97	.01	.02
$2a_1$	-.462	-.01	-.01	.74	.29	.00
$3a_1$	-.366	.50	.07	.15	.28	.01
$4a_1$	-.563	.00	.00	.50	.00	.00
$1b_1$	-.456	.01	.00	.92	.06	.01
$2b_1$	-.435	-.01	-.01	.82	.20	.00
$3b_1$	-.255	.35	.12	.17	.35	.01
$4b_1$	-.541	.01	.01	.49	.00	.00
Total Population		.85	.19	8.72	1.18	.06

TABLE 4.

The energy barrier, ΔE , for the reaction $\text{Ni}_2 + \text{H}_2 \rightarrow 2\text{NiH}$
 at the hydrogen distance, $R_3 = 1.06 \text{ \AA}$ and $d = 1.48 \text{ \AA}$.

Energies in electron volts.

	SCF ($^3\text{B}_1$)	SCF (4 electron)	GVB (4 electron)
ΔE	1.22	1.67	1.20

Figure 1.

Geometry of the Ni_2H_2 complex. The H_2 bond length varies from $R_1 = 0.74 \text{ \AA}$ to $R_2 = 2.49 \text{ \AA}$. $d = 1.48 \text{ \AA}$.

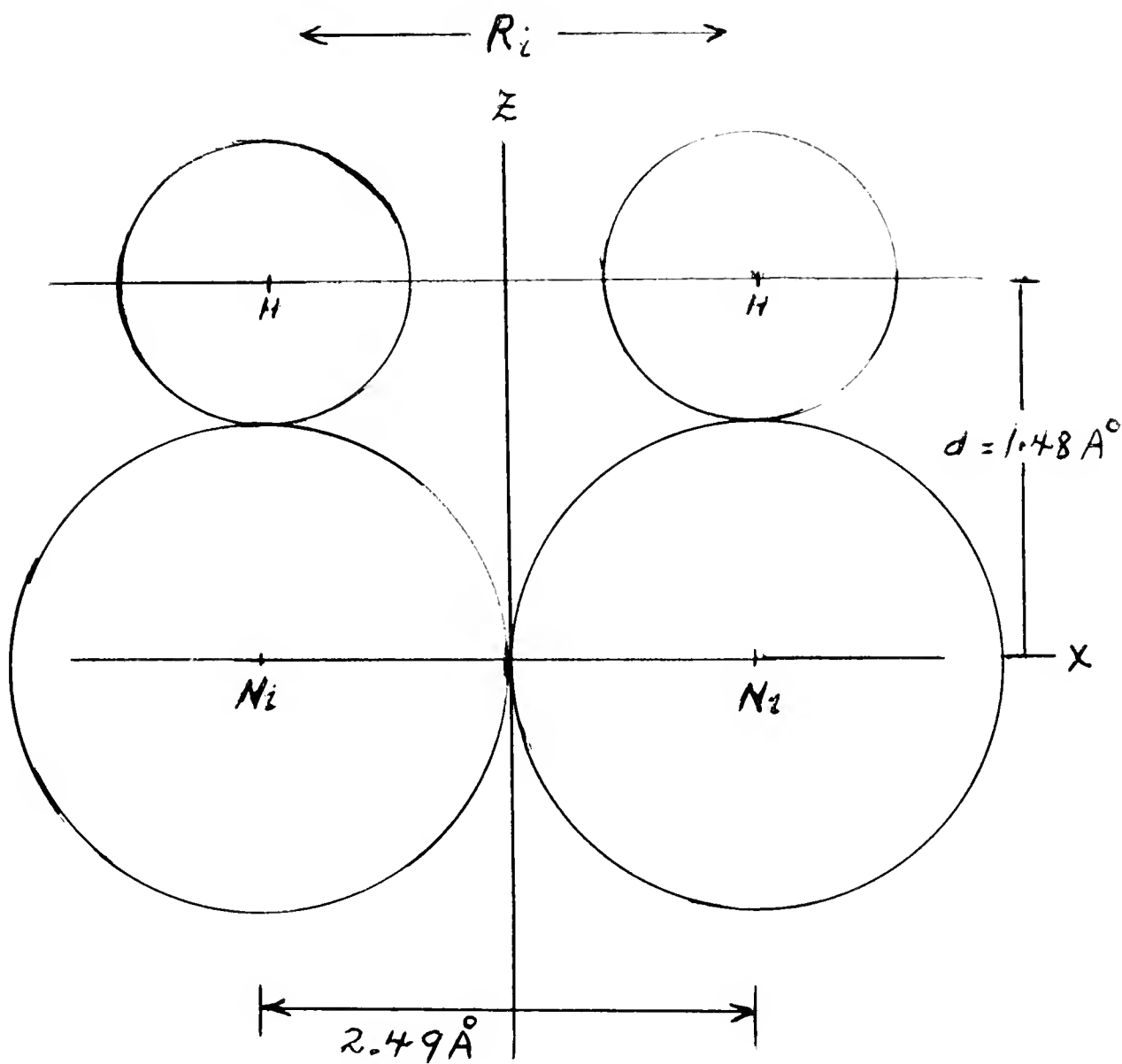


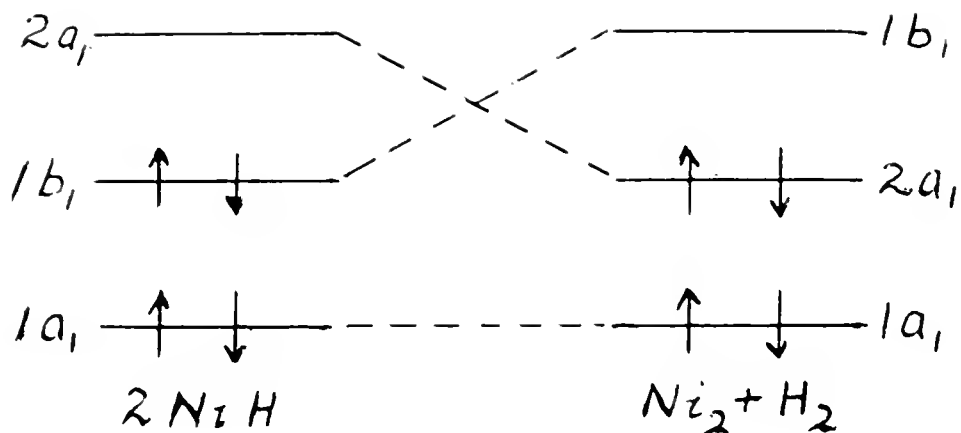
Figure 2.

Correlation diagram in the four electron model for the reaction,
 $\text{Ni}_2 + \text{H}_2 \rightarrow 2\text{NiH}.$

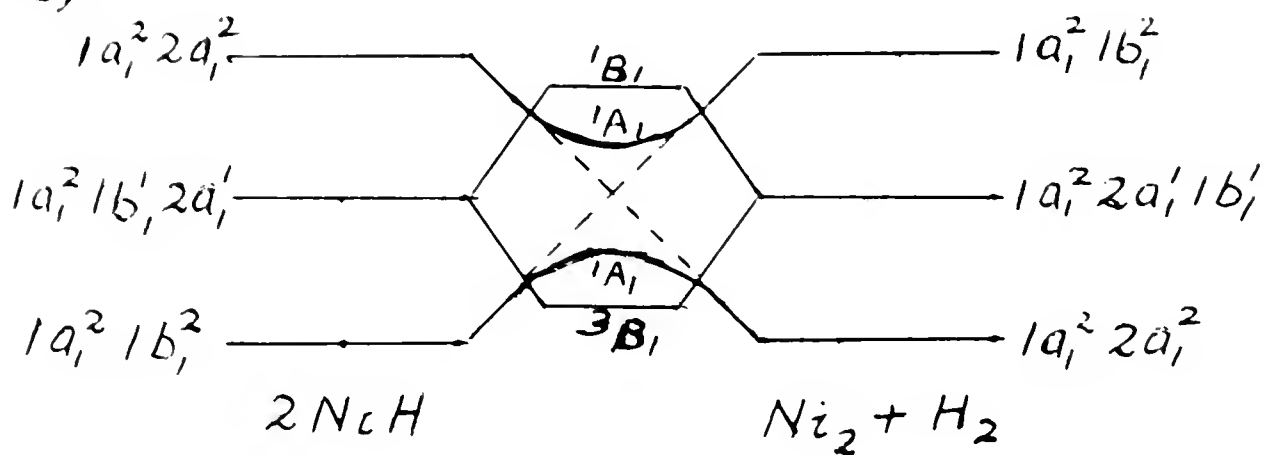
a) Orbital correlation diagram.

b) State correlation diagram.

a)



b)



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